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Thermal degradation of $BaAl_2Si_2O_8:Eu^{2+}$ phosphor excited by near ultraviolet light

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Eu^{2+}doped $BaAl_2Si_2O_8$ phosphor was synthesized by one-step calcination of precursors that were prepared by chemical co-precipitation. The thermal degradation properties of $BaAl_2Si_2O_8:Eu^{2+}$ were investigated by photoluminescence, lifetime and chromaticity coordinate measurements. $BaAl_2Si_2O_8:Eu^{2+}$ is efficiently excited by incident light of 250–400 nm, which matches the emission of near ultraviolet LED chips well. $BaAl_2Si_2O_8:Eu^{2+}$ exhibits broad blue emission at 470 nm because of the $4f^65d^1$-$4f^7$ ($^8S_{7/2}$) transition of Eu^{2+} ions, and the emission band shows an unusual blue shift with bandwidth broadening and emission intensity decreasing as the annealing temperature is increased. The luminescence decay and CIE chromaticity coordinates of $BaAl_2Si_2O_8:Eu^{2+}$ were determined to investigate its application in white LEDs.

thermal degradation, luminescence, aluminosilicate, phosphor

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In recent years, Eu^{2+}-activated phosphors have been intensively studied because their luminescent properties are suitable for use in solid-state lighting, e.g. white light emitting diodes (LEDs) fabricated with near ultraviolet (UV) chips [1–4]. The emission spectrum of Eu^{2+} ions is usually comprised of broad bands that range from UV to red regions caused by transitions between the $4f^7$ ground state and the crystal field components of the $4f^65d^1$ excited state configuration [5,6]. Emission is strongly dependent on the crystal fields of the host lattices because 5d orbitals are sensitive to the ligand field. Therefore, the choice of host affects the optical properties of Eu^{2+} ions significantly.

Aluminosilicate is well known as a long-persistent phosphor host with high chemical stability and water resistance. In alkaline-earth feldspars $MAl_2Si_2O_8$ (M=Ca, Sr, Ba), the framework structures are formed from an array of interlinked corner-sharing tetrahedral SiO_4 and AlO_4 species, with charge-compensating cations Ca^{2+}, Sr^{2+}, and Ba^{2+} occupying large cavities within the structure [7]. A series of solid solutions containing isostructural members with slightly different size cations as hosts [such as $MAl_2Si_2O_8$ (M=Ca, Sr, Ba)] would be an ideal system to study the effect of crystal chemical variation on the luminescence of Eu^{2+} ions, and may offer possibilities for commercial application [8].

Because the ability to withstand high temperature is required for phosphors in near-UV LEDs [9], the temperature-dependent luminescence properties of phosphors have attracted great attention. In this paper, the thermal degradation mechanism of $BaAl_2Si_2O_8:Eu^{2+}$ ($BAS:Eu^{2+}$) is explored. The lifetime and CIE chromaticity coordinates of $BAS:Eu^{2+}$ are also investigated.

1 Experimental

The phosphor $Ba_{1-x}Eu_xAl_2Si_2O_8$ (x=0.025) was prepared by

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chemical co-precipitation. $Ba(NO_3)_2$ (analytical reagent (A.R.), Kelong), $Al(NO_3)_3 \cdot 9H_2O$ (A.R., Kelong), Na_2SiO_3 (A.R., Kelong) and Eu_2O_3 (99.99%, Kelong) were used as raw materials. First, 0.00125 mol Eu_2O_3 was added to concentrated nitric acid and heated to give $Eu(NO_3)_3$. 0.0975 mol $Ba(NO_3)_2$, 0.2 mol $Al(NO_3)_3 \cdot 9H_2O$ and 0.2 mol Na_2SiO_3 were separately dissolved in deionized water and then mixed with the solution of $Eu(NO_3)_3$. The mixture was stirred and heated at 353 K for 1 h, and then an appropriate amount of precipitator (NH_4HCO_3 (A.R., Kelong)) was added. BAS:Eu^{2+} was obtained after the resulting precipitate was isolated, dried at 373 K for several hours, and then calcined at 1473 K for 2 h in a reducing atmosphere. To investigate the effect of the annealing process, samples were annealed at 623, 723, 823 and 923 K in air for 30 min. Emission and excitation spectra and decay curves were determined using a Hitachi F-4600 fluorescence spectrophotometer. The chromaticity coordinates of the BAS:Eu^{2+} phosphors were measured on a photoelectric color integrated test system (HSP-6000, HongPu).

2 Results and discussion

2.1 Luminescent characteristics

Photoluminescence excitation and emission spectra of BAS:Eu^{2+} (2.5 at%) are shown in Figure 1. The room temperature excitation spectrum of BAS:Eu^{2+} phosphor shows a broad band from 250 to 400 nm, which can be attributed to the 4f-5d transition of Eu^{2+} ions. The emission spectrum shows a single strong broad band centered at 470 nm, which is ascribed to the $4f^6 5d^1$-$4f^7(^8S_{7/2})$ transition of Eu^{2+} ions. Generally, the Stokes shift of Eu^{2+} emission is defined as the difference between the energy of the $4f^7(^8S_{7/2})$-$4f^6(^7F_0)5d^1$ transition and the emission energy [10]. Usually, the zero phonon line is defined as the intersection of the normalized absorption with the emission spectrum (416 nm, 2.9804 eV) [11]. According to the above definition, the Stokes shift for BAS:Eu^{2+} was calculated to be 0.7589 eV. In addition, no characteristic emission from Eu^{3+}, which exhibits a sharp peak between 560 and 630 nm, is observed in Figure 1(b), indicating that Eu^{3+} ions in the host were completely reduced to Eu^{2+} under a reducing atmosphere. Because the phosphor exhibits intense blue luminescence under excitation with UV light (250–400 nm), BAS:Eu^{2+} could potentially be used as a blue phosphor excited by a near-UV LED.

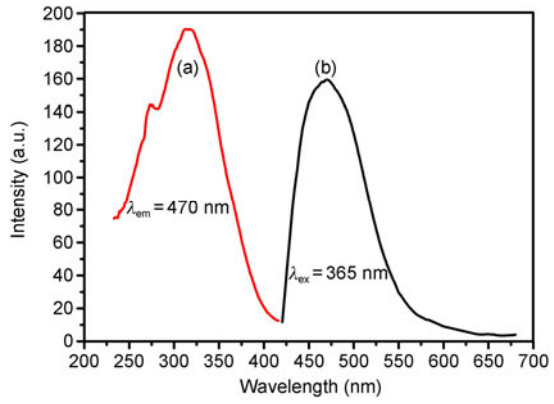

Figure 1 (Color online) (a) Photoluminescence excitation and (b) emission spectra of BAS:Eu^{2+}.

2.2 The effect of annealing temperature on the emission intensity of $BaAl_2Si_2O_8$:Eu^{2+}

In general, the temperature dependence of phosphors used in phosphor-conversion white LEDs is important because it has a considerable influence on the light output and color rendering index. Temperature-dependent luminescence spectra of BAS:Eu^{2+} (2.5 wt%) samples annealed at various temperatures upon excitation at 365 nm are presented in Figure 2. As the annealing temperature increased, the intensity of emission from Eu^{2+} ions at 470 nm decreased, and the characteristic red emission peak from the $^5D_0$-$^7F_2$ transition of Eu^{3+} centered at about 611 nm was observed. The thermal degradation mechanism of BAS:Eu^{2+} is explained by the following equation:

$$2Eu^{2+} + \frac{1}{2}O_2(g) + V_0 \rightarrow 2Eu^{3+} + O_0^{2-} \quad (1)$$

where Eu^{2+} is a divalent europium ion, $O_2(g)$ is a gaseous oxygen molecule, V_0 is an oxygen vacancy, Eu^{3+} is a trivalent europium ion, and O_0^{2-} is an oxygen ion in the lattice. During annealing, the oxidation mechanism involves three different processes: (1) The adsorption of a gaseous oxygen atom in an oxygen vacancy in the phosphor lattice. In this case, the adsorbed oxygen is not of the same valence as that of an oxygen ion in the phosphor lattice. To be stabilized, the adsorbed oxygen atom needs to accept electrons. Adsorption obviously occurs at the phosphor surface. (2) Diffusion of Eu^{2+} ions through the conduction layer caused by the increased temperature during thermal treatment. (3) Electronic transfer from a divalent europium ion to an adsorbed oxygen atom when the two species are close to each other [12]. As depicted in Figure 2(a), as the annealing temperature increases, the intensity ratio of the red emission (Eu^{3+}) to the blue emission (Eu^{2+}) increases because of electronic transfer from Eu^{2+} ions to adsorbed oxygen atoms (which accepts two electrons to achieve an O^{2-} valence state). Furthermore, excited luminescent centers are thermally activated through phonon interactions, which cause thermal release through the crossing point between the excited and ground states according to a configuration coordinate diagram [13]. The probability of this nonradiative transition by thermal activation is strongly dependent on temperature, and results in a decrease of emission intensity as the temperature increases. The thermally activated luminescent centers interact strongly with thermally active phonons,

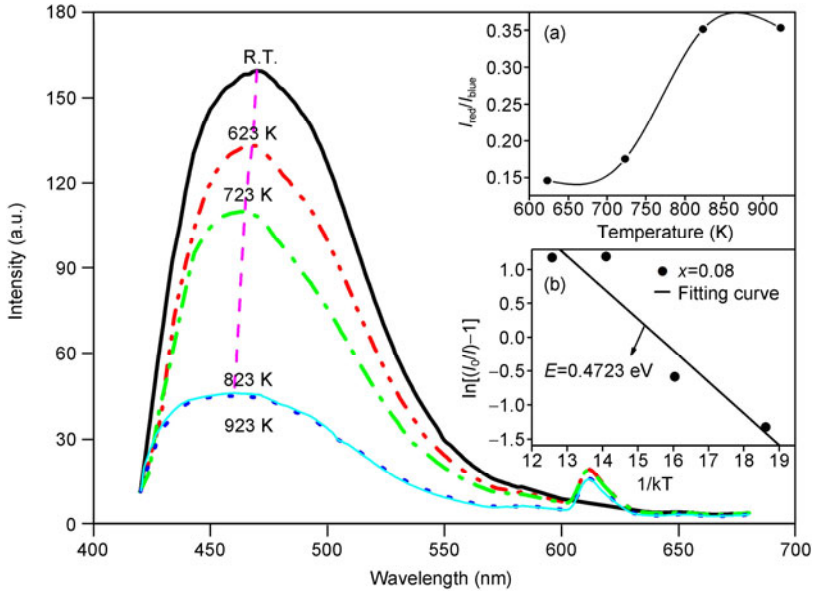

Figure 2 (Color online) Effect of annealing temperature on the luminescence intensity of BAS:Eu^{2+}. (a) The effect of annealing temperature on I_{red}/I_{blue},; (b) a plot used to find the activation energy for thermal quenching.

contributing to the full width at half maximum (FWHM) of the emission spectrum. At higher temperature, the density of phonons increases, and electron-phonon interactions dominate, so the FWHM of the emission spectrum increases, as depicted in Figure 2. In addition, a slight blue shift of the emission band is observed for the phosphors as the temperature increases. This can be explained by thermally activated phonon-assisted excitation from lower energy sublevels to higher energy sublevels in excited states of Eu^{2+}. To understand the temperature dependence of luminescence intensity and determine the activation energy for thermal quenching, the Arrhenius equation was fitted to thermal quenching data:

$$I(T) \approx \frac{I_0}{1 + c\exp\left(\frac{-E}{\mathrm{kT}}\right)}, \tag{2}$$

where I_0 is the initial intensity, $I(T)$ is the intensity at a given temperature T, c is a constant, E is the activation energy for thermal quenching, and k is the Boltzmann constant. A plot of $\ln[(I_0/I)-1]$ versus $1/(\mathrm{kT})$ is presented in Figure 2(b). E, which fits all of the data closely, is 0.4723 eV for BAS:Eu^{2+}.

2.3 The effect of annealing temperature on the lifetime of $BaAl_2Si_2O_8$:Eu^{2+}

The decay curves for BAS:Eu^{2+} samples annealed at different temperatures are shown in Figure 3. The curves can be well fitted using the double-exponential equation [14]:

$$I = A\exp\left(-t/\tau'\right) + B\exp\left(-t/\tau''\right), \tag{3}$$

where τ' and τ'' are fast and slow components of decay, respectively, and A and B are fitting parameters. The average lifetime (τ) can be determined as $\tau=(A\tau'^2+B\tau''^2)/(A\tau'+\tau'')$, as shown in Figure 3(b). The lifetime for blue Eu^{2+} emission at room temperature was calculated to be about 128.1 ms. As the annealing temperature increases, the lifetime of Eu^{2+} decreases. This can be attributed to defect traps being formed by the movement of Eu ions during heat treatment. These results agree with those reported by Zhang et al. [15].

2.4 The effect of annealing temperature on the CIE chromaticity coordinate of $BaAl_2Si_2O_8$:Eu^{2+}

The chromaticity diagram established by the Commission Internationale de l'Eclairage (CIE) in 1931 is a two-dimensional graphical representation of colors perceived by the human eye. Figure 4 shows the CIE chromaticity coordinates of the samples excited at 365 nm at various temperatures (623–923 K). As the annealing temperature of the phosphor increased, the CIE coordinate shifted slightly from (0.1687, 0.1571) to (0.1950, 0.1392), which is consistent with the observed blue shift of the emission peak and the increased emission from Eu^{3+} (Figure 2). However, the change in CIE with temperature is indistinct. All of the CIE chromaticity coordinates are in the blue region.

3 Conclusions

The BAS:Eu^{2+} phosphor was prepared by chemical co-precipitation, and its luminescent properties were investigated in detail. As the temperature used to anneal the sample was

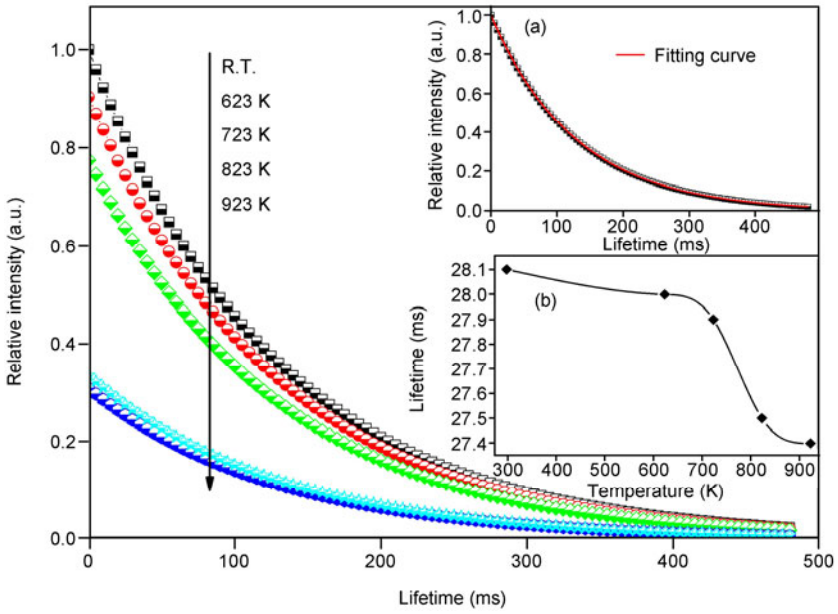

Figure 3 (Color online) Decay curves of 470 nm emission from Eu^{2+} ions at different annealing temperatures. (a) The fitting curve of the unannealed sample; (b) the temperature dependence of the lifetimes of the samples.

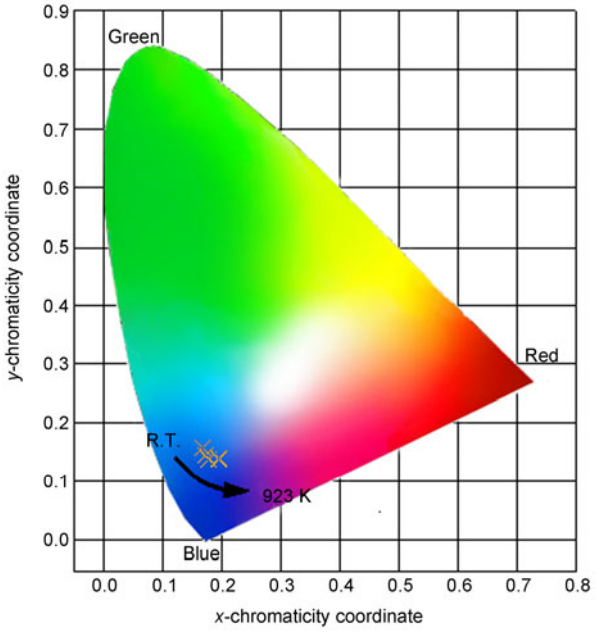

Figure 4 (Color online) CIE chromaticity coordinates of BAS:Eu^{2+} phosphors excited at 365 nm at various temperatures.

increased, the emission bands showed an anomalous blue shift along with increasing bandwidth and decreasing intensity. The temperature dependence of this blue shift can be described in terms of back tunneling from excited states of the low-energy emission band to excited states of the high-energy emission band through the assistance of thermally active phonons. The lifetime of emission remains nearly constant with increasing temperature. Because of its excitation band in the near-UV region, intense blue emission, high thermal luminescence stability and appropriate chromatic coordinates, this BAS:Eu^{2+} phosphor is expected to be a promising candidate for near-UV LEDs.

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